

optimal laser pulse design for transferring the coherent nuclear wave packet of H_2^+

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Within the Franck-Condon approximation, the single ionization of H_2 leaves H_2^+ in a coherent superposition of 19 nuclear vibrational states. We numerically design an optimal laser pulse train to transfer such a coherent nuclear wave packet to the ground vibrational state of H_2^+ . The simulation results show that the population of the ground state after the transfer is more than 91%. Frequency analysis of the designed optimal pulse reveals that the transfer principle is mainly an anti-Stokes transition, *i.e.* the H_2^+ in $1s\sigma_g$ with excited nuclear vibrational states is first pumped to $2p\sigma_g$ state by the pulse at an appropriate time, and then dumped back to $1s\sigma_g$ with lower excited or ground vibrational states.

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I. INTRODUCTION

Controlling coherent quantum states has been a long-standing goal since the invention of laser pulses. With the rapid advent of technology in recent years [1], researchers can now fine-tune the laser parameters to control the ultrafast processes inside atoms and molecules [2–4]. For example, by varying the relative phase of a two-color (ω - 3ω) laser field with ω the fundamental angular frequency, the target molecule may be constructively or destructively excited by simultaneously absorbing the ω and 3ω photons [5]. Another example is to change the time delay between two laser pulses so that the molecule can be first pumped to an intermediate state, then evolves and accumulates the time-dependent phases, and later be dumped to a different final state, thereby changing the production of a chemical reaction [6]. Furthermore, specific tailoring of the laser field may dictate a complex chemical reaction to follow one particular channel and stay away from all the others, achieving a selective terminal state [7]. Most recently, thanks to the phase-stabilized few-cycle laser pulse [8], the emission of an ionized electron [9], or the charge-direct transfer between nuclei [10, 11] also become possible. The attosecond pulse may be used to selectively excite or ionize the target at unprecedentedly precise timing during the chemical reactions [12–14], and thus helps understanding the time-resolved fundamental physics.

As the simplest neutral molecule, H_2 (or D_2) is often chosen as a prototype system to be controlled and analyzed. In the past few decades, the basic processes for H_2 exposed in strong laser fields have been extensively studied. As shown in Fig. 1, after one electron absorbs enough photon energy and escapes from the nuclei, it is left with a molecular ion H_2^+ in $1s\sigma_g$ state [15]. From

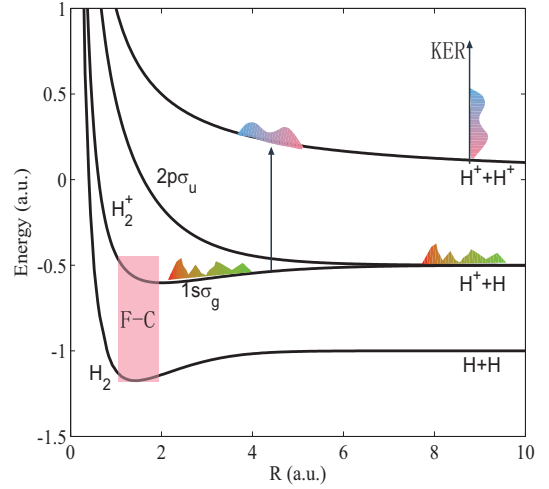


FIG. 1: (Color online) The schematic picture for the interaction between laser pulses and H_2 . Four curves from bottom up are the potential curves for H_2 , H_2^+ in $1s\sigma_g$, H_2^+ in $2p\sigma_u$, and coulomb explosion. F-C remarks the Franck-Condon transition area. The single ionization of H_2 produces the H_2^+ in $1s\sigma_g$, followed by the dissociative ionization by the probe pulse. The kinetic energy release (KER) reflects the information when the coulomb explosion happens.

the Franck-Condon approximation [16], we can assume that initially the nuclear wave packet (NWP) of H_2^+ is the same as the ground state of H_2 , and then it evolves along the $1s\sigma_g$ potential curve, as shown in Fig. 2(c) [17]. If a time-delayed probe pulse is subsequently introduced, H_2^+ may dissociate through the laser-induced coupling between $1s\sigma_g$ and $2p\sigma_u$ [11, 18–21]. The mixture of the dissociative channels, *i.e.* the paired and unpaired states, will induce an asymmetric electron localization [12, 22–31]. Alternatively, H_2^+ may also be ionized by the probe pulse, which leads to the Coulomb explosion [15, 32]. The internuclear distance when the ionization of H_2^+ tak-

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ing place can be reflected by the kinetic energy release (KER) of the Coulomb-explosion fragments [33–36]. In addition to these non-electron correlation processes, the first ionized electron may come back and rescatter with H_2^+ , accompanying with the excitation of H_2^+ [37, 38] and high harmonic generation [39], or auto-ionization [40]. If the laser environments are appropriate, the single ionization of H_2 may leave the H_2^+ in higher excited electronic states, *e.g.* $2p\sigma_u$ [14] or $2p\pi_u$ [41].

In these processes, the complexity of the H_2^+ NWP makes the whole process even more complicated. After the single ionization, the NWP of H_2^+ is a superposition of 19 vibrational states with negligible auto-dissociative states. Each vibrational state has a different spatial distribution. Once the molecule is dissociated or ionized, each vibrational state also contributes a different KER to the molecular fragments [42]. The coherent superposition of the vibrational states may partly smear the asymmetric electron localization [31], or lead to the time-dependent dissociation [43]. Since the stationary nuclear state can significantly simplify the physical picture, it is often desired to transfer the coherent NWP to one stationary state, especially to the ground vibrational state of H_2^+ .

For the hetero-nuclear molecular ion HD^+ , the permanent dipole induced by the asymmetric nuclear mass may transfer the Franck-Condon NWP to the ground vibrational state [44]. However, for H_2^+ , the external laser field has to be applied. Niederhausen and Thumm suggested to use the multi-pulse protocol to control the Franck-Condon coherent NWP and found that in the final coherent population, the largest proportion for a certain vibrational state can exceed 60% [45]. Niikura *et al.* studied to exert a laser-induced dipole force at an appropriate time to achieve up to 50% population for the ground vibrational state [46]. Picon *et al.* proposed to use a chirped few-hundred-femtosecond pulse or pulse train to transfer the first and second excited vibrational states to the ground vibrational state with the proportion up to 90% [47]. Bryan *et al.* used the pump-modify-probe strategy to manipulate the vibrational states, where the time-delayed second pulse may modify the relative populations of different states [48].

In this paper we use optimal control theory to numerically design a laser pulse train to tailor the coherent vibrational states. We formulate it as a minimax problem with bounded constraints, and then apply sequential linear programming algorithm [49] to solve it. The gradient of the performance metric with respect to the laser pulses can be derived in an analytic manner, which facilitates the numerical computation. For the initial Franck-Condon NWP, the transfer to the ground vibrational state is achieved with the population more than 91%.

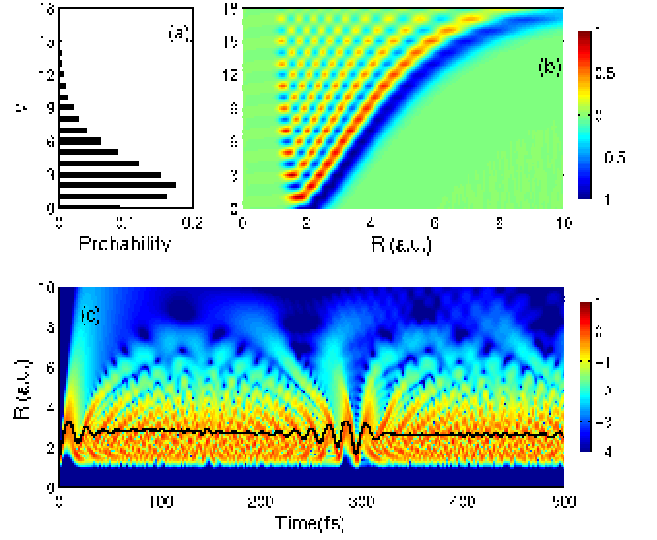


FIG. 2: (Color online) (a) Franck-Condon coefficients of the NWP of H_2^+ . (b) Wave functions for the 19 vibrational states (in linear scale). (c) The free propagation of the Franck-Condon NWP of H_2^+ in the $1s\sigma_g$ potential curve (in logarithmic scale).

II. NUMERICAL MODEL

A. Two-state equation

Consider the case that the single ionization of H_2 produces a free electron and a molecular ion H_2^+ in $1s\sigma_g$, where the NWP of H_2^+ is described by the Franck-Condon approximation. If the time-delayed probe pulse is introduced to cause the dissociation, the dynamics is mainly governed by a two-state equation (atomic units are used unless otherwise stated)

$$i \frac{\partial}{\partial t} \begin{bmatrix} \psi_g(R, t) \\ \psi_u(R, t) \end{bmatrix} = \begin{bmatrix} T_R + V_g(R) & d_{gu}(R)E(t) \\ d_{gu}(R)E(t) & T_R + V_u(R) \end{bmatrix} \begin{bmatrix} \psi_g(R, t) \\ \psi_u(R, t) \end{bmatrix}, \quad (1)$$

where $\psi_g(R, t)$, $\psi_u(R, t)$ are the NWP corresponding to the electron in $1s\sigma_g$ and $2p\sigma_u$ states, and $V_g(R)$, $V_u(R)$ are the potential curves for $1s\sigma_g$ and $2p\sigma_u$ states, respectively. The dipole coupling between these two states is represented by d_{gu} , and $T_R = -\frac{1}{2M} \frac{\partial^2}{\partial R^2}$ is the second order differential operator, where $M = 918$ is the reduced mass of two nuclei. The molecular rotation is neglected since we limit the pulse duration within a few tens of femtoseconds. The initial NWP is given by

$$\psi_g(R, 0) = \psi_{\text{Gr}}^0(R), \quad \psi_u(R, 0) = 0, \quad (2)$$

where $\psi_{\text{Gr}}^0(R)$ is the ground state of H_2 . We use the Split-Operator method to solve Eq. (1) [50]. The R spans from 0 to 40, and the spatial step $\Delta R = 0.04$. The time step is set as $\Delta t = 1$. Mask functions are used to suppress the unphysical reflection by the boundary of the simulation box.

Our objective is to design a laser pulse E such that at the terminal time T_f , ψ_g can be transferred to the ground state of H_2^+ , *i.e.*

$$\psi_g(R, T_f) = \psi_g^{\nu=0}(R), \quad (3)$$

where ν is the index of the vibrational state. The initial NWP $\psi_g(R, 0)$ is mainly a superposition of 19 vibrational states. By projecting it to the vibrational eigenstates of H_2^+ , we obtain the Franck-Condon coefficients, as shown in Fig. 2(a). The three vibrational states $\nu = 1, 2$, and 3 amount to around 50% of the total population. Fig. 2(b) shows the wave function for all these 19 vibrational states, and Fig. 2(c) plots $|\psi_g(R, t)|^2$. The black curve in Fig. 2(c) is the expected time-dependent internuclear distance $\langle R(t) \rangle$. Clearly, the NWP goes through a collapse and revival procedure, and the revival time is about 300 fs [15, 17].

B. Numerical optimization algorithm

We formulate the design of a laser field E to realize the NWP transfer of ψ_g as a minimax problem, and then apply a sequential linear programming algorithm to solve it. To avoid ionization of H_2^+ , we restrict the amplitude of E within 0.1, and the pulse duration less than 32 fs.

The wave function transfer is formulated as a constrained minimax problem on the laser electric field E :

$$\min_E \max_{n \in \{0, 1, \dots, N-1\}} J_n, \quad (4)$$

subject to

$$|E(t_k)| \leq 0.1, \quad k = 0, \dots, K-1, \quad (5)$$

where

$$J_n = \frac{1}{2} \left\| \psi_g^0(R_n) - e^{-i\alpha} \psi_g(R_n, T_f) \right\|^2. \quad (6)$$

Here n (or k) is the index for the spatial (or temporal) step, N (or K) is the total points in the spatial (or temporal) axis, and α is a global phase to be determined soon. The function J_n quantifies the difference between the desired and actually achieved wave functions at the spatial grid R_n . If the maximum error of J_n is minimized over the whole spatial range, one can expect that the desired wave function is achieved.

The NWP transfer fidelity can be measured by

$$F = \text{Re} \{ e^{i\alpha} \langle \psi_g(R, T_f) | \psi_g^{\nu=0}(R) \rangle \}. \quad (7)$$

The global phase α in Eqs. (6) and (7) can be obtained by maximizing the fidelity:

$$\alpha = -\arg \{ \langle \psi_g(R, T_f) | \psi_g^{\nu=0}(R) \rangle \}, \quad (8)$$

where \arg denotes the argument of a complex number.

The minimax problem has been extensively studied in the optimization and control community [51–53]. To find

the optimal laser field, we start from an initial guess and then gradually approach the optimal solution by iteration. Suppose that at the j -th iteration, the current laser pulse is E^j . We need to determine a small increment ΔE^j such that at the $(j+1)$ -th step, the new laser pulse $E^{j+1} = E^j + \Delta E^j$ is a better solution to minimize the transfer error J_n . By first order approximation, we have

$$J_n(E^{j+1}) \approx J_n(E^j) + \nabla_{E^j}^T J_n(E^j) \Delta E^j. \quad (9)$$

The analytic derivation of the gradient $\nabla_{E^j}^T J_n(E^j)$ is given in the appendix.

We then apply a sequential linear programming algorithm as follows:

1. Choose a small constant as the initial guess of the electric field;
2. At the j -th step, compute $J_n(E^j)$ and $\nabla_{E^j} J_n(E^j)$;
3. Determine the increment ΔE^j from the following linear programming problem:

$$\min_{\Delta E^j} \gamma,$$

subject to

$$\begin{aligned} \nabla_{E^j}^T J_0(E^j) \Delta E^j + J_0(E^j) &\leq \gamma, \\ &\vdots \\ \nabla_{E^j}^T J_{N-1}(E^j) \Delta E^j + J_{N-1}(E^j) &\leq \gamma, \\ -0.1 - E^j &\leq \Delta E^j \leq 0.1 - E^j. \end{aligned}$$

4. Let $E^{j+1} = E^j + \epsilon \Delta E^j$, where ϵ is a small positive number controlling the step size;
5. Repeat Steps (2)–(4) until a desired convergence is reached.

Note that in each iteration we only need to solve a linear programming problem, which can be readily calculated by numerical packages.

III. OPTIMAL DESIGN RESULTS

Starting from $E(t) = 0.01$, after around 12,000 iterations and 350+ hours computation on a desktop computer with Intel i5 CPU, we have obtained a satisfactory optimal laser pulse as shown in Fig. 3(a). Fig. 3(b), (c), (d) show the optimal laser pulse induced NWP evolution for $|\psi_g(R, t)|^2$, $|\psi_u(R, t)|^2$, and $|\psi_g(R, t)|^2 + |\psi_u(R, t)|^2$, respectively.

Fig. 3(a) reveals an interesting physical story. First of all, the optimal laser field is a pulse train. After the inception of H_2^+ , nearly no electric field is introduced until $t = 11$ fs. In this period, the NWP propagates freely to the outer turning point and then turns back, as shown in

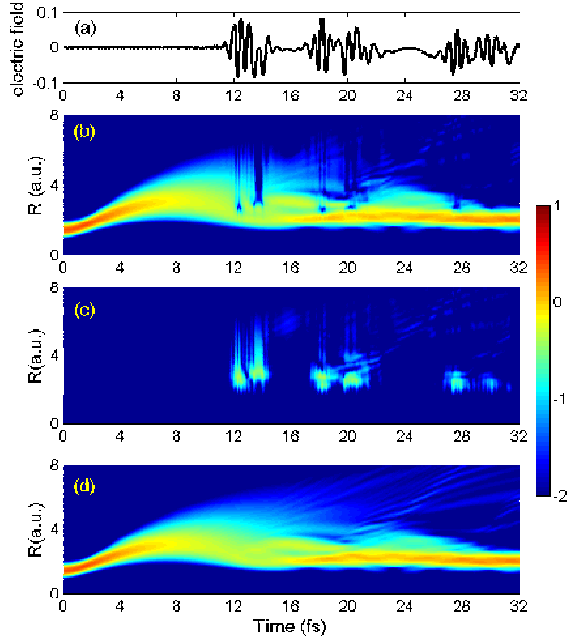


FIG. 3: (Color online) (a) The designed optimal laser pulse train. The evolution of $|\psi_g(R, t)|^2$ (b), $|\psi_u(R, t)|^2$ (c), and $|\psi_g(R, t)|^2 + |\psi_u(R, t)|^2$ (d) (all in logarithmic scale).

Fig. 3(b). The main pulse appears at around $t = 11$ fs, at which time the NWP is moving inward instead of outward. This is important because if the laser field starts interacting with the NWP when it is moving outward, part of the wave packets will directly dissociate and the subsequent laser pulse has little chance to pull them back to the bound states [46].

To transfer $\psi_g(R, t)$ to $\psi_g^{\nu=0}(R)$, $\psi_u(R, t)$ must be mediated. From a closer look at Fig. 3(b) and (c), one may find that within each oscillation of the electric field, part of ψ_g and ψ_u are exchanged. The wave function $\psi_u(R, t)$ mainly distributes close to the range $R = 3$. The quantity $|\psi_g(R, t)|^2 + |\psi_u(R, t)|^2$ gives a smooth evolution of the NWP, as depicted in Fig. 3(d). At the terminal time, the NWP has been transferred to the ground vibrational state.

To gain a deeper understanding of the transfer principle, we trace the time-dependent probability evolution of each individual vibrational state, which can be written as

$$P_\nu(t) = |\langle \psi_g^\nu(R) | \psi_g(R, t) \rangle|^2, \quad \text{for } \nu = 0, \dots, 18. \quad (10)$$

Fig. 4 shows $P_\nu(t)$ for the first seven vibrational states. It is clear that the population of $\nu = 0$ increases to 91% at the end of the evolution, and the staircase jumps take place at the times when the laser pulse is introduced. The quick increasing of the ground state population and the precipitous dropping of the excited vibrational states indicate that the laser induced coupling is roughly an anti-Stokes transition: H_2^+ with higher nuclear vibrational

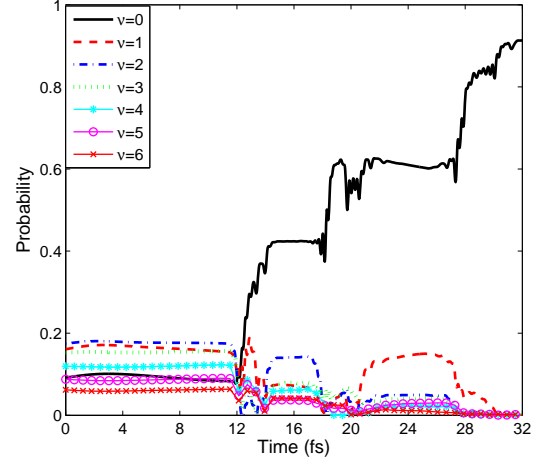


FIG. 4: (Color online) The time-dependent probabilities for the lowest 7 vibrational states.

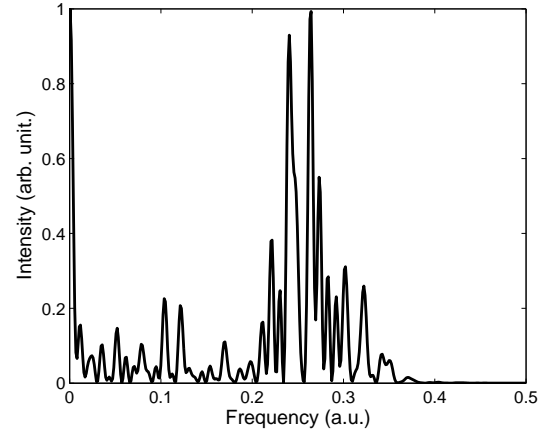


FIG. 5: The frequency spectrum for the designed optimal laser pulse train.

states is excited from $1s\sigma_g$ to $2p\sigma_u$, and then de-excited to $1s\sigma_g$ with lower nuclear vibrational states. The probability evolution details show more physical scenarios. At the beginning $\nu = 1$ and $\nu = 2$ states have similar probabilities. After the first laser pulse, the probability of $\nu = 1$ is halved, whereas the probability of $\nu = 2$ does not change much. Surprisingly, after the second pulse, the probability of $\nu = 1$ is doubled and is much larger than that of $\nu = 2$. After these two pulses, the vibrational states with $\nu \geq 2$ are already very small, and the upcoming third pulse mainly transfers $\nu = 1$ to $\nu = 0$. During the whole process, $\nu = 1$ state works as a temporary reservoir for storing some population, for ultimately maximizing the population of $\nu = 0$.

The frequency spectrum of the obtained laser pulse train is shown in Fig. 5 after performing the Fourier transform. The main frequency component is around 0.25. This is consistent with the optimization result in

Fig. 3(c), where $\psi_u(R)$ is mainly excited at the internuclear distance between 2.5 to 3, for the energy gap between $1s\sigma_g$ and $2p\sigma_u$ at the corresponding internuclear distance is around 0.25. The frequency analysis demonstrates that the multi-frequency laser pulse train pumps and dumps H_2^+ with different frequency components.

IV. CONCLUSIONS

In conclusion, by restricting the laser pulse duration to less than 32 fs and confining the electric amplitude within 0.1, we numerically design an optimal laser pulse train to successfully transfer the initial Franck-Condon NWP to the ground vibrational state of H_2^+ with a population 91%, and the dissociation probability is only 9%. The optimal laser pulse train does not act on the NWP until the NWP is moving inward. The field-induced Raman transition between $1s\sigma_g$ and $2p\sigma_u$ transfers the highly excited vibrational states to $\nu = 0$ directly, or indirectly first to $\nu = 1$ but finally to $\nu = 0$ state. This control algorithm can be extended to other molecules.

Acknowledgments

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Appendix: Derivation of $\nabla_{Ej} J_n$

For completeness, we first briefly describe the numerical procedure to solve the Schrödinger equation (1). We follow the standard split-operator techniques in Refs. [50, 54, 55]. Let

$$E = [E_0, E_1, \dots, E_{K-1}], \quad R = [R_0, R_1, \dots, R_{N-1}].$$

The solution of Eq. (1) can be written as

$$\psi(R, T_f) = \prod_{k=0}^{K-1} e^{-iH_k \Delta t} \psi(R, 0), \quad (\text{A.1})$$

where

$$H_k = \begin{bmatrix} T_R + V_g(R) & d_{gu}(R)E_k \\ d_{gu}(R)E_k & T_R + V_u(R) \end{bmatrix},$$

which is decomposed as

$$H_k = T + G_k,$$

where

$$T = \begin{bmatrix} T_R & 0 \\ 0 & T_R \end{bmatrix}, \quad G_k = \begin{bmatrix} V_g(R) & d_{gu}(R)E_k \\ d_{gu}(R)E_k & V_u(R) \end{bmatrix}.$$

The propagation operator $e^{-iH_k \Delta t}$ in Eq. (A.1) can be calculated by the split-operator method:

$$e^{-iH_k \Delta t} = e^{-iT \frac{\Delta t}{2}} e^{-iG_k \Delta t} e^{-iT \frac{\Delta t}{2}} + O(\Delta t^3). \quad (\text{A.2})$$

Substitution of Eq. (A.2) into Eq. (A.1) yields

$$\psi(R, T_f) = e^{-iT \frac{\Delta t}{2}} \left(\prod_{k=0}^{K-1} e^{-iG_k \Delta t} e^{-iT \Delta t} \right) e^{iT \frac{\Delta t}{2}} \psi(R, 0). \quad (\text{A.3})$$

Here the terms $e^{-iT \frac{\Delta t}{2}}$ and $e^{-iT \Delta t}$ can be calculated by Fast Fourier Transform (FFT) [54]. Since all the four blocks in G_k are diagonal matrices, we can transform G_k into a block diagonal matrix $\bar{G}_k = \text{diag}\{G_k^0, G_k^1, \dots, G_k^{N-1}\}$, where

$$G_k^n = \begin{bmatrix} V_g(R_n) & d_{gu}(R_n)E_k \\ d_{gu}(R_n)E_k & V_u(R_n) \end{bmatrix}. \quad (\text{A.4})$$

Because G_k^n is symmetric, it can be derived that

$$e^{-iG_k^n \Delta t} = \exp \left\{ -i \frac{V_g(R_n) + V_u(R_n)}{2} \Delta t \right\} \left\{ \cos \frac{\theta_k \Delta t}{2} I - i \sin \frac{\theta_k \Delta t}{2} \left(\frac{V_g(R_n) - V_u(R_n)}{\theta_k} \sigma_z + \frac{2d_{gu}(R_n)E_k}{\theta_k} \sigma_x \right) \right\}, \quad (\text{A.5})$$

where σ_x, σ_z are Pauli matrices, and

$$\theta_k = \sqrt{(V_g(R_n) - V_u(R_n))^2 + (2d_{gu}(R_n)E_k)^2}. \quad (\text{A.6})$$

This completes the numerical solution of Eq. (1).

Now from Eq. (6), we have

$$\begin{aligned} \nabla_E J_n = & -\text{Re} \left\{ \left(\bar{\psi}_g^0(R_n) - e^{i\alpha} \bar{\psi}_g(R_n, T_f) \right) \right. \\ & \left. \times \nabla_E (e^{-i\alpha} \psi_g(R_n, T_f)) \right\}. \end{aligned} \quad (\text{A.7})$$

For an element E_k in the vector E , it is easy to get

$$\begin{aligned} & \frac{\partial}{\partial E_k} e^{-i\alpha} \psi_g(R_n, T_f) \\ &= e^{-i\alpha} \frac{\partial}{\partial E_k} \psi_g(R_n, T_f) - e^{-i\alpha} \psi_g(R_n, T_f) \frac{\partial \alpha}{\partial E_k}. \end{aligned} \quad (\text{A.8})$$

From Eqs. (A.3), we obtain that

$$\begin{aligned} & \frac{\partial}{\partial E_k} \psi(R, T_f) = e^{-iT \frac{\Delta t}{2}} \left(\prod_{l=k+1}^{K-1} e^{-iG_l \Delta t} e^{-iT \Delta t} \right) \\ & \times \frac{\partial}{\partial E_k} e^{-iG_k \Delta t} e^{-iT \Delta t} \left(\prod_{l=0}^{k-1} e^{-iG_l \Delta t} e^{-iT \Delta t} \right) e^{iT \frac{\Delta t}{2}} \psi(R, 0). \end{aligned}$$

From Eqs. (A.5) and (A.6), it follows that

$$\frac{\partial}{\partial E_k} e^{-iG_k^n \Delta t} = \frac{\partial}{\partial \theta_k} e^{-iG_k^n \Delta t} \frac{\partial \theta_k}{\partial E_k} + \frac{\partial}{\partial E_k} e^{-iG_k^n \Delta t}.$$

Proceeding further, we obtain

$$\begin{aligned} \frac{\partial}{\partial \theta_k} e^{-iG_k^n \Delta t} &= e^{-i\frac{V_g+V_u}{2}\Delta t} \left\{ -\frac{\Delta t}{2} \sin \frac{\theta_k \Delta t}{2} I \right. \\ &\quad - \frac{i\Delta t}{2} \cos \frac{\theta_k \Delta t}{2} \left(\frac{V_g - V_u}{\theta_k} \sigma_z + \frac{2d_{gu}E_k}{\theta_k} \sigma_x \right) \\ &\quad \left. + i \sin \frac{\theta_k \Delta t}{2} \left(\frac{V_g - V_u}{\theta_k^2} \sigma_z + \frac{2d_{gu}E_k}{\theta_k^2} \sigma_x \right) \right\}, \end{aligned}$$

and

$$\begin{aligned} \frac{\partial \theta_k}{\partial E_k} &= \frac{4d_{gu}^2 E_k}{\theta_k}, \\ \frac{\partial}{\partial E_k} e^{-iG_k^n \Delta t} &= -ie^{-i\frac{V_g+V_u}{2}\Delta t} \sin \frac{\theta_k \Delta t}{2} \frac{2d_{gu}}{\theta_k} \sigma_x. \end{aligned}$$

Lastly, we need to calculate $\frac{\partial \alpha}{\partial E_k}$ in Eq. (A.8). Reread-

ing Eq. (8) and defining

$$\begin{aligned} p &= \text{Re} \left\{ \sum_{n=0}^{N-1} \psi_g^0(R_n) \overline{\psi_g(R_n, T_f)} \right\}, \\ q &= \text{Im} \left\{ \sum_{n=0}^{N-1} \psi_g^0(R_n) \overline{\psi_g(R_n, T_f)} \right\}, \end{aligned}$$

we obtain

$$\frac{\partial \alpha}{\partial E_k} = \frac{1}{p^2 + q^2} \left(p \frac{dq}{dE_k} - q \frac{dp}{dE_k} \right),$$

where $\frac{dp}{dE_k}$ and $\frac{dq}{dE_k}$ are none other than the real and imaginary parts of the quantity

$$\sum_{n=0}^{N-1} \psi_g^0(R_n) \frac{\partial}{\partial E_k} \overline{\psi_g(R_n, T_f)}.$$

Combining all these equations, we can calculate $\nabla_{E_j} J_n$ in an explicit manner.

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